

## XAS Study of Au Supported on $\text{TiO}_2$ : Influence of Oxidation State and Particle Size on the Catalytic Activity

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*We investigated the effect of synthesis, pre-treatment, and reaction conditions on the structure, activity, and oxidation state of Au clusters supported on nanocrystalline and mesoporous  $\text{TiO}_2$ . X-ray absorption spectroscopy was applied to correlate the particle size and oxidation state with several parameters, such as the pH of the precursor solution, Au loading, pre-treatment, and support structure. Catalytic CO oxidation activity data were obtained and correlated with the particle size, indicating a decrease of activity with particle growth. In-situ studies of Au supported on different allotropic forms of  $\text{TiO}_2$  revealed that the high activity state corresponds to Au in a fully reduced state.*

Catalysis by small gold particles has been the object of considerable attention in the past few years. The reactivity of gold (Au) was found to be tunable for many important reactions, such as CO oxidation, through the control of particle size and the selection of support materials. It is generally accepted that the Au particle structure and the consequent catalytic properties depend on the support used, Au loading, the synthesis method, and pre-treatment conditions. Among various supports, reducible oxides, such as  $\text{TiO}_2$ , are perhaps the most popular due to the expected strong metal-support interaction phenomena they exhibit. Our goal was to vary many of these factors and characterize the gold supported on titania, during preparation and the working state, using x-ray absorption spectroscopy (XAFS). We scrutinized Au supported on different allotropic nanocrystalline forms of titania and on mesoporous titania material. The XAFS data at the Au  $L_{\text{III}}$ -edge were collected at beamline X18B in transmission and fluorescence mode using a channel cut Si (111) monochromator.

The effect of Au loading on the particle size and reducibility of Au clusters was studied using mesoporous  $\text{TiO}_2$  as a support. The most important observation was that lower Au loadings resulted in bigger Au aggregates with lower reducibility. The x-ray absorption near-edge structure (XANES) provided information regarding changes in the Au oxidation state during in-situ pre-treatment and reaction conditions. Varying the titania crystalline structure does not seem to affect the

redox behavior of the Au clusters.

For instance, during the study of Au supported on anatase, a gradual reduction of the Au precursor was clearly observed when the reaction mixture, 1% CO/air, was present at room temperature (**Figure 1a**), even though the concentration of oxygen is 20 times higher than the reductant. Once fully reduced in  $\text{H}_2$ , no re-oxidation occurs under reaction conditions, even after flowing air at higher temperatures (**Figure 1b**).



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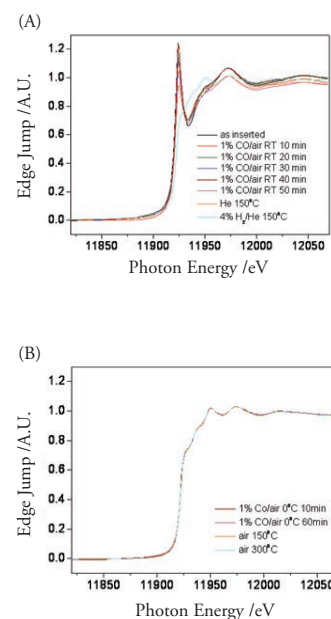
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These observations imply that reaction conditions also drive the sample irreversibly towards the fully reduced state. Furthermore, a comparison of lightoff curves after exposing a single sample to a sequence of pretreatment steps demonstrated that Au is in a highly active state, in the form of Au<sup>0</sup>, after treatment in H<sub>2</sub> at 150°C. This indicates that oxidized Au is not necessary for high activity.

A comparison of the activity for CO oxidation and the mean particle size determined by extended x-ray absorption fine structure (EXAFS) is provided in **Figure 2**. The activity is described using T<sub>50</sub>, the temperature at which the conversion reaches 50%. The particle size is estimated using the hemispherical cuboctahedron model given the Au-Au first shell coordination number, which is obtained directly from the EXAFS. By these measures, we see that there is a correlation between the Au particle size in the range studied and the activity. Data are given for each sample following the treatment in H<sub>2</sub> at 150°C and following treatment in O<sub>2</sub> at 300°C. Although the catalytic activities of Au supported on these different allotropic forms of titania are comparable after low temperature treatments, the stability of the Au-catalysts at higher temperatures is dependent upon the TiO<sub>2</sub> structure-type. Au on brookite exhibited no significant particle agglomeration and was the most active catalyst after treatment at 300°C.



Figures 1A and 1B. XANES of the Au supported on anatase after different pretreatment protocols.

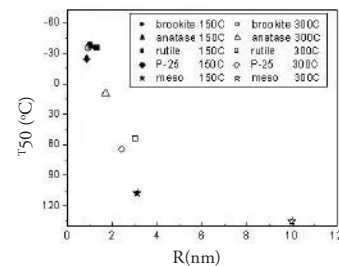


Figure 2. Relationship between activity on CO oxidation and particle size.